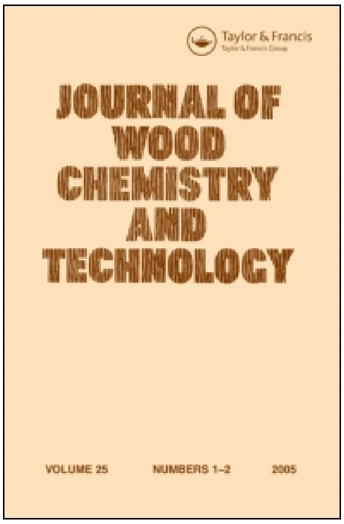

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RAMAN SPECTRAL FEATURES ASSOCIATED WITH CHROMOPHORES IN HIGH-YIELD PULPS

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ABSTRACT

High-yield pulp chromophores are not easily analysed. In Raman spectroscopic studies, advantage can be taken of the fact that chromophores absorb visible light, and they are therefore expected to result in manifestation of the resonance Raman effect. In this effect, the Raman scattering coefficient depends upon the wavelength used to excite the spectrum. The contribution of chromophores in the spectra of mechanical pulps was identified by recording Raman spectra excited at two different wavelengths (514.5 and 647.1 nm). In these spectra, the intensities of certain bands and the band width of the 1595 cm^{-1} band changed when the wavelength of excitation was changed. These changes were clear evidence of the presence of the chromophores and useful indicators of the extent to which the chromophores were present in the mechanical pulps. Spectral contributions due to chromophores were found at 1120, 1595, 1620, and 1654 cm^{-1}. Raman studies of bleached pulps were consistent with these observations and indicated that chromophores were not completely removed by the bleaching processes.

INTRODUCTION

The brightness of high-yield pulps is largely determined by the light-absorption characteristics of pulp constituents. Cellulose and other carbohydrates do not absorb in the visible region of the spectrum.[1] The role of other pulp constituents, namely lignin and components that are not readily extractable, such as metal complexes and organic matter occluded in the carbohydrate matrix, is not well-defined. A number of structures belonging to either class have the capability of acting as chromophores[2,3] and therefore are likely to be responsible for lower brightness.

Only a few techniques are useful for *in situ* studies of color-causing structures in high-yield pulps because the amounts of individual chromophore species are very low and the types of structures capable of light absorption are many. Past studies have relied primarily on UV-visible spectroscopy to study the chromophores. However, this technique has had limited success in this application because the amount of detail in the spectra does not allow the development of sufficient information about the molecular structures of the chromophores. Raman spectroscopy can provide important complementary structural information that will add to understanding of the chromophores.

We have applied Raman spectroscopy in studies of wood and pulp samples. The results of such studies have indicated that the technique provides information that is sensitive to the molecular structures of various constituents of a sample.[4-6] For example, in the Raman spectra of wood samples, certain spectral features related to lignin were found to be intensity enhanced.[7] Further studies on this topic showed that the enhancement arises from two distinct effects, namely, resonance Raman (RR) processes and conjugation effects (CEs). These phenomena reflect different manners of dependence of the Raman scattering coefficients on the molecular structure of scattering species. The RR phenomenon, in particular, can substantially increase the intensities of vibrational bands. Such an enhancement depends primarily upon a sample's ability to absorb light at the wavelength of excitation.[8] The CE, on the other hand, is independent of the frequency of excitation and enhances the band intensity to a lesser extent.[9] This effect is caused by π electron conjugated bond systems that do not absorb light at the wavelength of excitation. The relative contributions of the two enhancement mechanisms can be distinguished because the RR effect varies with the frequency of excitation while the CE is independent of excitation wavelength. Thus, the presence and resolution of the contributions of these effects in the Raman spectra of wood samples can provide information on the presence and nature of aromatic ring-conjugated structures and chromophores in the samples.

In the case of thermomechanical pulp (TMP) chromophores, the application of the Raman technique has appeared promising because the chromophores are light-absorbing and likely to show resonance enhancement. Moreover, since their contribution depends upon the frequency of laser excitation, spectral contributions specific to chromophores can be identified. The main objective of the present work was to analyse Raman spectral data on high-yield pulps in terms of contributions from both the nonabsorbing structures in lignin and the light-absorbing structures (chromophores). Such a separation of contributions may be arbitrary since the structures representing chromophores may also be part of lignin. Nevertheless, because the spectral contributions from these two types of structures will have different sensitivities towards the variation of excitation wavelength, it is advantageous to resolve the total Raman scattering signal in terms of contributions from the two disticnt groups of components.

In the present study, an unbleached TMP sample and additional TMP samples bleached by three different procedures were chosen for investigation by Raman spectral methods. The three bleached pulps differed with regard to the extent to which the chromophores were modified and/or removed as compared to the unbleached TMP. Because bleaching by the methods used primarily affected the chromophores and left the other components largely intact, the pulps remained quite rich in lignin. The contributions of chromophores to the Raman spectra were distinguished by comparing spectra of bleached and unbleached pulps. The information in these features was further developed by comparing spectra recorded with two different excitation wavelengths.

EXPERIMENTAL

Pulp Samples

Unbleached spruce TMP was provided by Consolidated Papers Inc., Wisconsin Rapids, Wisconsin. The TMP was bleached reductively ($NaBH_4$) and also in two separate multistage oxidation-reduction treatments. Reductive bleaching was carried out by treating TMP with 0.5 M $NaBH_4$ for 4 days at room temperature;this pulp will be referred to as $NaBH_4$ pulp. Some of the TMP was bleached in two stages using a peroxide-hydrosulfite system. Peroxide bleaching of the pulp was carried out by using 8% H_2O_2 (on pulp) in aqueous alkali for 4 h in the presence of sodium silicate and magnesium sulfate. The initial pH of the liquor was 10.5. After the treatment, the pulp was washed until all the excess alkali was removed. In the second stage, the peroxide-bleached pulp was treated by a 2% hydrosulfite solution at 70°C for 1 h. The pulp was extensively washed after the treatment. This pulp will be referred to as H_2O_2-hydrosulfite pulp. Some of this pulp was further bleached in a third stage using a 0.5 M $NaBH_4$ solution. The three-stage bleached pulp will be referred to as HP-HS-BH pulp.

The unbleached and bleached pulps were studied by Raman spectroscopy. The mechanical pulps were also analysed for lignin content, and their brightness values were measured. Lignin content was determined using the Klason method (T222 om-83).[10] Tappi method T525 om-86[10] was used to measure diffuse brightness on a Technibrite TB-1 instrument.

Raman Spectroscopy

Raman spectra were obtained using an Instruments S A Ramanor HG2S spectrometer. This computer-controlled scanning instrument has a photomultiplier tube as a detector. Both the 514.5 nm line from an argon ion laser and the 647.1 nm line from a krypton ion laser were used for sample excitation. The lasers were operated in the light control mode to keep the power output constant. The spectral region 250-3700 cm^{-1} was studied. Pulps were sampled as handsheets in the standard 90° sampling-geometry mode. To quench sample fluorescence, the pulps were kept in an atmosphere of molecular oxygen[11]. The method involves exposing a laser-irradiated sample to either a stream of oxygen or to oxygen at high pressure (345 kPa). A Raman spectrum can be acquired after significant quenching of the background has occurred. Multiple scans were accumulated to improve the signal-to-noise ratio in the spectra. Reported spectra are averages of multiple scans. In most cases, the averaged spectrum contained a broad background as a result of a residual fluorescence signal. Such a contribution from the spectrum was removed by subtracting a mathematically generated curve that parallels the fluorescence background. This also facilitated study of weak features in the spectra.

RESULTS AND DISCUSSION

The Raman spectra of the pulps, in the region between 850 and 1850 cm^{-1}, are shown in Figure 1 (excited with the 514.5 nm laser line) and Figure 2 (excited with the 647.1 nm line). The peak intensity and band-width data are summarized in Table 1, and pulp brightness data appear in Table 2. Although the Raman spectra were recorded over a wider frequency range (250-3700 cm^{-1}),

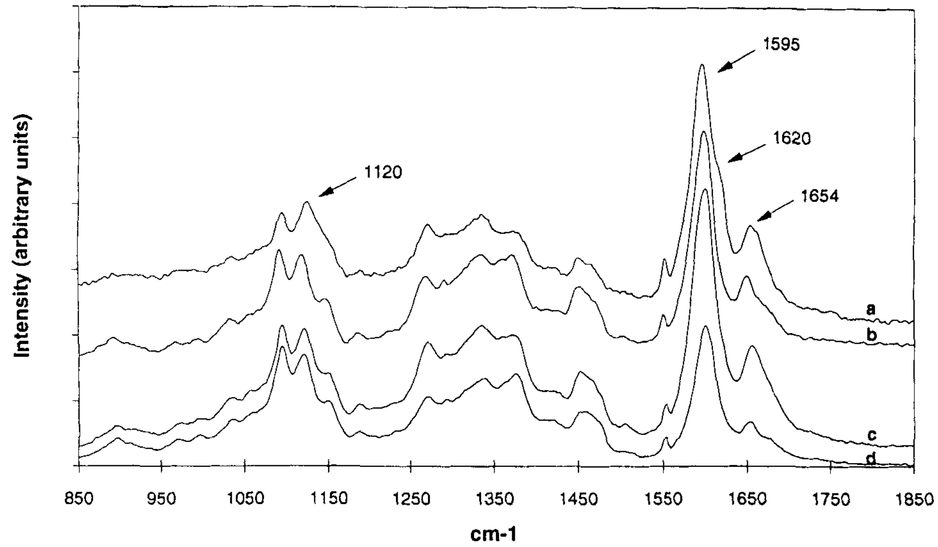

Figure 1—514.5 nm excited Raman spectra of spruce pulps: (a) unbleached pulp, (b) $NaBH_4$ bleached, (c) H_2O_2-hydrosulfite bleached pulp, and (d) peroxide-hydrosulfite-borohydride (HP-HS-BH) bleached pulp. The 1550 cm^{-1} peak in spectrum (b) is due to molecular oxygen. Spectra have been shifted to avoid overlapping. Intensity scale is arbitrary.

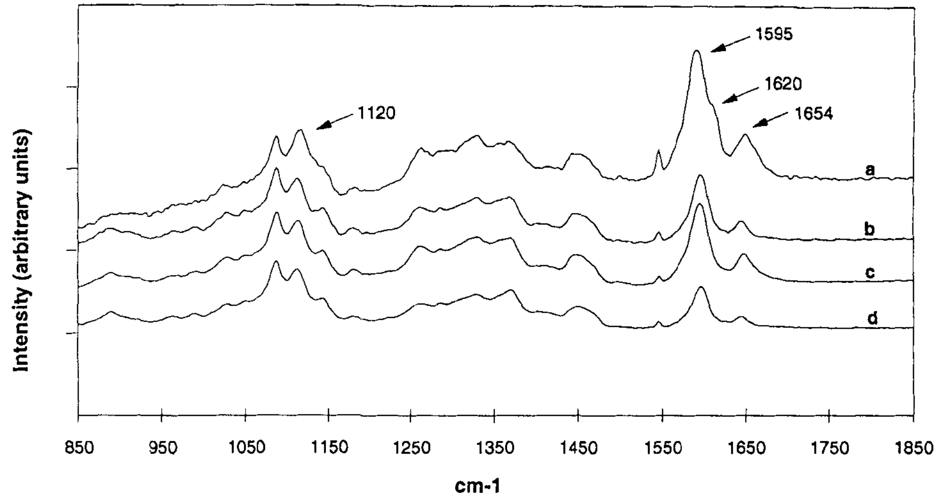

Figure 2—647.1 nm excited Raman spectra of spruce pulps: (a) unbleached, (b) $NaBH_4$ bleached, (c) H_2O_2-hydrosulfite bleached, and (d) HP-HS-BH bleached. See Figure 1 caption for other explanatory notes.

TABLE 1
Raman Intensities and FWHM Data of Spruce Pulps at Two Excitation Wavelengths[a]

Excitation wavelength (mm)	Spectral feature[b]	Unbleached pulp	Bleached pulp		
			$NaBH_4$	H_2O_2-hydrosulfite	HP-HS-BH[c]
514.5	FWHM(cm^{-1})	39	31	33	31
	I(1120)	1.16	0.93	0.92	0.89
	I(1595)	3.65	2.18	2.50	1.35
	I(1620)	2.04	0.78	1.05	0.60
	I(1654)	1.30	0.69	1.00	0.40
647.1	FWHM(cm^{-1})	39	25	25	23
	I(1120)	1.04	0.83	0.85	0.86
	I(1595)	2.49	1.30	1.64	0.90
	I(1620)	1.57	0.43	0.58	0.22
	I(1654)[d]	0.96	0.40	0.65	0.26

[a] Full-width-at-half-maximum (FWHM) data are from the 1595 cm^{-1} band.

[b] I(wavenumber) is relative intensity of band with respect to 1098 cm^{-1} band of cellulose.

[c] HP-HS-BH is hydrogen peroxide-hydrosulfite-borohydride.

[d] Instrument response factor used for this band was same as that for the 1620 cm^{-1} band.

TABLE 2
Difference in Resonance Raman Contributions (Band Intensity Reductions) Between 514.5- and 647.1-nm Laser Excitation and Other Pulp Data

Pulp	Reduction in band intensity (%)[a]				Klason lignin (%)	Brightness (%)
	1120	1595	1620	1654		
Unbleached	10	32	23	34	28.6	52.1
$NaBH_4$	11	25	35	42	27.4	71.3
H_2O_2-hydrosulfite	8	34	45	35	27.8	75.2
HP-HS-BH	3	33	63	35	25.0	77.7

[a] Bands identified by wavenumber (cm^{-1}).

chromophore-related changes occurred only in the 850-1850 cm^{-1} spectral region.

Band Assignments

To place the present work in perspective, it is useful to review assignment of the relevant features in the Raman spectra. The Raman spectra of lignin have been reported in greater detail elsewhere,[12,13] so we confine ourselves here to discussion of those features that can be related to chromophoric species. As we will note, these features include contributions to the bands at 1120, 1595, 1620, and 1654 cm^{-1}.

The chromophore groups considered to be present in lignin are coniferaldehyde, α-ketones, and o- and p-quinones.[2,3] In some cases, however, the supporting evidence is not conclusive and further research is needed. Considering that the information on the nature of chromophores in lignin and pulps is incomplete, it is possible that additional chromophores are present. The Raman contributions due to such structures could possibly arise at one or more of the four band positions that have been identified in this work. Nonetheless, these bands can be assigned to known Raman contributions of some chromophores in lignin.

The band at 1139 cm^{-1} in softwood lignin spectra has been assigned to the aromatic C-H in plane bending vibration. This is also a main peak position in the coniferaldehyde Raman spectrum (authors' unpublished results). In the work described here, the 1120 cm^{-1} band is likely to reflect contributions from this mode of vibration. The most intense Raman band in pulp and lignin spectra is at 1595 cm^{-1}; it is a result of a symmetric aromatic ring stretching mode.[12] Since lignin has many aromatic structural units, it is likely that more than one species contributes at or near this frequency. It is therefore not possible to identify the particular contributions of the individual species. The vibrational mode involving the aromatic-ring-conjugated C=C group is known to contribute as a shoulder at 1620 cm^{-1} in coniferaldehyde structures and as a separate band at 1654 cm^{-1} in coniferyl alcohol structures.[13] Finally, the 1654 cm^{-1} band also has contributions from the coniferaldehyde carbonyl groups in lignin.[13] In the instance of the coniferaldehyde, the C=C band is shifted to 1620 cm^{-1} due to coupling effects.

The coniferaldehyde group (a chromophore in lignin) can be easily detected in the Raman spectra of pulps. However, contributions that could be associated with α-carbonyl and quinone groups were not detected at the expected wavenumber positions (α-carbonyl 1670 cm^{-1}, o-quinone 1555 cm^{-1}, p-quinone 1650 and 1680 cm^{-1}; these are based on the authors' unpublished work on lignin models). It is to be noted that p-quinone has two Raman bands and both must be detected if its presence is to be postulated. It is possible that one or another of these groups is present at sufficiently low concentrations that its contribution cannot be distinguished in the presence of the bands associated with the dominant components.

Spectral Comparisons

Spectral differences arising both from bleaching and from change in excitation wavelength are summarized in Table 1 and are shown in Figures 1 and 2. Spectra in Figure 1 were obtained using 514.5 nm excitation; spectra in Figure 2 were obtained using the ion laser line at 647.1 nm for excitation. Table 1 lists relative intensities of the Raman bands of interest relative to the intensity of the 1098 cm^{-1} band, which is due to cellulose and is used as the internal reference. The base-line method has been used to calculate band intensities. The table also includes full-width-at-half-maximum (FWHM) data for the 1595 cm^{-1} band. Contributions to the FWHM data from the neighboring 1620 band cm^{-1} could not be resolved readily; therefore, the data are for the convoluted-profile centered at 1595 cm^{-1}. Table 2 shows the percentage of reduction in intensity of Raman bands upon changing excitation to longer wavelengths; these values are the measure of the contribution of the RR effect.

Spectral Differences Arising Upon Bleaching—Upon bleaching, pulp chromophores, including those that are integrated into the lignin, undergo significant changes. The structure of lignin, on the other hand, is only modified to the extent that the small amounts associated with chromophore units are modified or removed. In this study, the lignin content of the pulps (Table 2) was consistent with this expectation; only small variations within lignin content were detected. Therefore, in comparisons of the spectra excited at the same wavelength, the intensity changes at 1120, 1595, 1620, and 1654 cm^{-1} must be representative of structural modifications in lignin and removal of other pulp chromophores, the latter being chromophores other than those in lignin; for example, metal complexes[3] or yet-unknown structures in pulp. Except for the Raman band at 1120 cm^{-1}, carbohydrates do not contribute at these wavenumbers. Moreover, carbohydrates remain largely unmodified during bleaching treatments such as those applied.

The lowest chromophore-associated intensities were observed for the brightest pulp (Table 1, HP-HS-BH data). In addition, the decline in the FWHM of the 1595 cm^{-1}, which occurred for all bleached pulps, was greatest for the brightest pulp. Furthermore, for constant wavelength excitation, band intensities and FWHM values depended upon the nature of the bleached pulp. The extent to which bleached pulps differed from one another seems to depend on the nature of the chemical treatments. For example, both the $NaBH_4$ and the HP-HS-BH bleached pulps gave identical FWHM values for the 514.5 nm wavelength, although the HP-HS-BH pulp had lower intensities for both the 1595 and 1620 cm^{-1} bands (Table 1). Such intensity reductions, along with the decline at 1120 cm^{-1}, suggest that the $NaBH_4$ treatment did not completely remove coniferaldehyde structures and that these structures were more efficiently removed in the HP-HS-BH treatment. The identical FWHM value seen in the HP-HS-BH pulp may have arisen from yet-unidentified changes and was a mere coincidence. These observations are also supported by the 647.1 nm wavelength data (Table 1).

Spectral Changes Dependent Upon Excitation-Wavelength—To assign observed intensity and band-width changes to either chromophore-free lignin or chromophores, whether or not these changes are an integral part of the lignin, the total changes need to be separated in terms of individual contributions. Such a separation of contributions can be achieved by varying the wavelength of the exciting radiation. The results of such studies are summarized in Tables 1 to 3. The reported relative intensity data for excitation with the 647.1 nm laser line have been corrected for the instrument response. The data for the 1654 cm^{-1} band were corrected using the instrument factor for the 1620 cm^{-1} band. The two data sets are directly comparable. The differences in RR contributions to band intensities between green and red laser line excitations are reported in Table 2. For all the pulps, the data in Tables 1 and 2 indicate that the band intensities for all four bands declined when the excitation wavelength was changed from 514.5 to 647.1 nm.

For the unbleached pulp, the observed reduction in intensity of the four Raman bands with change in excitation wavelength from 514.5 to 647.1 nm (Table 2) indicates that structures capable of absorbing green light contribute to band intensity. Such chemical structures are, by definition, chromophores. This interpretation is supported by Raman data on the bleached pulps. As noted earlier, the spectra of the bleached pulps showed reduced intensities for the four bands (Table 1, 514.5 nm data; band intensities in columns 4 to 6 are lower than corresponding intensities in column 3). Reduction in band intensities upon bleaching is also supported by the data obtained using the red laser line (Table 1, 647.1 nm data).

The FWHM data for the 1595 cm^{-1} band (Table 1) represent changes in the profile of the band. For the bleached pulps, the 647.1 nm excitation gave lower FWHM values. Lower values imply that upon red line excitation, certain chromophores that were responsible for the original band-width (514.5 nm excited FWHM data) no longer contributed to the same extent. This observation is supported by the bleached pulp data (Table 1), which show narrowing of the band upon removal of the chromophores (lower FWHM values). Thus, the band-width data also indicate that the 1595 and 1620 cm-1 features have contributions from the chromophores in pulps.

Although, as a result of bleaching, the contributions of the chromophores to the Raman spectra were reduced to varying degrees, the contributions were not completely removed. This can be noted from the RR data for bleached pulps in Table 2; band intensities of 1595, 1620, and 1654 cm^{-1} continued to decline with change in excitation line. The decline in band intensity indicates that absorbing species remain in the bleached pulps. This observation is further supported by the FWHM data in Table 1. For all bleached pulps, the FWHM values declined further when the 647.1 nm excitation was used (e.g., in Table 1, FWHM data for $NaBH_4$ pulp show a decline of 6 cm^{-1}). The data that indicate survival of some chromophores after all three bleaching sequences suggest that some chromophores may be unaccessible to the bleaching agents as a result of occlusion within nonswellable parts of the pulp fiber walls.

It is also interesting to note that red line excitation caused a significant decline in intensity of the 1595, 1620, and 1654 cm^{-1} bands (Table 2, 23%-63%), whereas the 1120 cm^{-1} band showed only a small decline (11%-3%). Very little change in this latter band was observed for the HP-HS-BH bleached pulp (Table 2, 3%). The low level of decline can be attributed to two factors. First, a major portion of the intensity at 1120 cm^{-1} is from carbohydrates (up to 77% in TMP; authors' unpublished data). Second, because the coniferaldehyde Raman

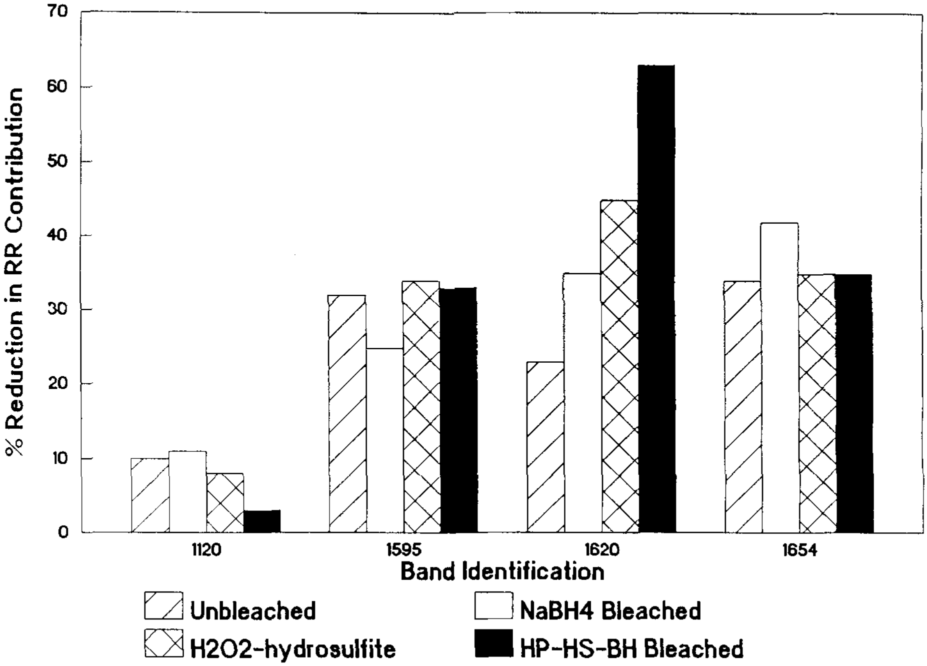

Figure 3—Graphic representation of data in Table 2. Amount of reduction in resonance Raman (RR) contributions for different pulps. Reductions shown for four Raman bands containing contributions from chromophores.

peak that contributes to 1120 cm^{-1} band is located at 1139 cm^{-1}, its contribution at 1120 cm^{-1} is minimal.

In summary, the data in Tables 1 and 2 clearly show that for a pulp sample, changes in Raman band intensities and FWHM, which are associated with changes in laser excitation wavelength, are caused by light-absorbing species. Depending upon the Raman band, band intensity changed from 3% to 63%. All four pulps clearly contained chromophores that absorb at 514.5 nm; otherwise, none of the bands would have declined when the excitation was changed to 647.1 nm.

The pattern of variation of band intensities is illustrated in Figure 3, in which data from Table 2 are plotted as bar graphs. In Figure 3, the 1620 cm^{-1} band of the HP-HS-BH bleached pulp shows the greatest reduction in the RR

TABLE 3
RR and CE Contributions to Bleaching-Related Reduction in Band Intensity for 1595 cm^{-1} Band

	Reduction in band intensity (%)[a]		
Pulp	514.5 nm (RR+CE)	647.1 nm (RR+CE)	$(RR+CE)_{red} - (RR+CE)_{green}$[b]
$NaBH_4$	40	48	8
H_2O_2-hydrosulfite	32	34	2
HP-HS-BH	63	64	1

[a] RR is resonance Raman; CE is conjugation enhancement.
[b] Red excitation = 647.1 nm; green excitation = 514.5 nm.

effect (63%). In other words, in the case of HP-HS-BH pulp, the RR effect was much more subdued than was the case for the unbleached pulp; the latter showed only a change of 23% when the longer wavelength excitation was used. This indicates that the unbleached pulp contains chromophores that absorb light even at 647.1 nm.

On the basis of the changes in 1620 cm^{-1} band intensity, we expect that the order of the pulps, in terms of ability to absorb 514.5 nm light, would be as follows: unbleached >$NaBH_4$ bleached >H_2O_2-hydrosulfite bleached >HP-HS-BH bleached. This trend is consistent with the brightness data in Table 2. It is clear, therefore, that the RR contribution at 1620 cm^{-1} is correlated with pulp brightness. Since the other Raman bands do not show this trend (Table 2), it is clear that their intensities do indeed reflect contributions from unaffected structures. As was noted earlier, the contributions at 1120, 1595, and 1654 cm^{-1} can arise from more than one class of components. As a result, when the contributions of the chromophores are removed, the behavior of the band will depend upon relative-intensity contributions of the remaining components.

Table 3 summarizes the data for the RR and CE contributions to the reduction in intensity of the Raman band at 1595 cm^{-1} in the spectra of different pulps. Comparison of the data, which were obtained using the red and green excitations, reveals that the smallest difference between RR contributions (resulting from absorption by chromophores at 514.5 and 647.1 nm) exists in the spectra of bleached pulps. The percentage of reduction in band intensity (RR+CE) upon bleaching was calculated from data in Table 1. The actual difference in contribution could be higher than that shown in Table 3 (last column), but not less. These data indicate that the HP-HS-BH bleached pulp showed a higher difference in RR contribution than did either of the other bleached pulps, suggesting a larger differential absorption between 514.5 and 647.1 nm wavelengths for the HP-HS-BH pulp compared to the other bleached pulps. In contrast, the change in absorption between the wavelengths was small (column 3, Table 3) for the H_2O_2-hydrosulfite and HP-HS-BH pulps. In other words, the chromophores contributing to the 1595 cm^{-1} band in the $NaBH_4$ bleached pulp absorbed more light at 514.5 nm than did the chromophores in the other bleached pulps. This implies that the borohydride treatment is less effective than the two- and three-stage bleaching, an observation supported by the brightness data in Table 2. Similar analyses can be carried out for the remaining Raman bands, and differences between the RR contributions in differently bleached pulps can be calculated at 514.5 and 647.1 nm wavelengths.

Other Chemical Changes

For a chosen excitation wavelength, both the RR effect and the CE need to be considered in comparison of Raman data for bleached and unbleached pulps because the chemical treatments are likely to cause structural changes in both absorbing and nonabsorbing pulp species. However, to consider changes resulting from either species, their contributions need to be separated. This is important because if contributions from absorbing structures could be isolated, then chemical changes caused by bleaching in nonchromophoric structures could be evaluated. The bulk of pulp components consist of molecular structures that fall in the nonabsorbing category. With conventional Raman instrumentation—relying on visible wavelength excitation—such a separation cannot be accomplished. Sample excitation in near-infrared wavelength is required to avoid contributions resulting from the RR effect. Such an experimental requirement can now be met with the availability of FT-Raman instruments based on 1.06 µ Nd:YAG laser excitation.

CONCLUDING REMARKS

Raman spectroscopy can be used to study mechanical pulp chromophores. When excited with 514.5 nm laser light, chromophores exhibited resonance Raman (RR) effect. In the Raman spectra of mechanical pulps, chromophore contributions to band intensity were identified by varying the wavelength of laser excitation and by comparing spectral data of bleached and unbleached pulps. In the present work, chromophores contributed to bands at 1120, 1595, 1620, and 1654 cm^{-1}. Two important spectral parameters were the intensities of the Raman bands and the full-width-at-half-maximum value of the 1595 cm^{-1} band. In the case of bleached pulps, changes in these parameters indicated that chromophores were present even in extensively bleached pulps. The RR contributions at the 1620 cm^{-1} band correlated well with the brightness data of pulps.

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